



# Reaction kinetics of hydrothermal carbonization of loblolly pine



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## HIGHLIGHTS

- An innovative reactor was designed to measure hydrothermal reaction kinetics.
- At temperatures between 200 and 260 °C, weight loss kinetics are quite rapid.
- Reactions are modeled by parallel first-order degradation of hemicellulose and cellulose.
- Mass transfer and reaction kinetics may both be important.

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## ABSTRACT

Hydrothermal carbonization (HTC) is a pretreatment process to convert diverse feedstocks to homogeneous energy-dense solid fuels. Understanding of reaction kinetics is necessary for reactor design and optimization. In this study, the reaction kinetics and effects of particle size on HTC were investigated. Experiments were conducted in a novel two-chamber reactor maintaining isothermal conditions for 15 s to 30 min reaction times. Loblolly pine was treated at 200, 230, and 260 °C. During the first few minutes of reaction, the solid-product mass yield decreases rapidly while the calorific value increases rapidly. A simple reaction mechanism is proposed and validated, in which both hemicellulose and cellulose degrade in parallel first-order reactions. Activation energy of hemicellulose and cellulose degradation were determined to be 30 and 73 kJ/mol, respectively. For short HTC times, both reaction and diffusion effects were observed.

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## 1. Introduction

Because of the abundant renewable supply of lignocellulosic biomass, much research and development has been conducted to find economical means to utilize this feedstock for fuels, chemicals, and energy. More than a billion tons of dry lignocellulosic biomass is available in the US (Perlack and Stokes, 2011). Although lignocellulosic biomass is inexpensive, challenges, including diverse feedstocks, widely dispersed production, low calorific value, and seasonal availability, make biomass' handling and transportation expensive (Tester, 2005). Moreover, the chemical properties of lignocellulosic biomass make it even more unfavorable in traditional thermochemical applications. To overcome these challenges, there is a need for a process to homogenize the feedstocks and simultaneously produce a stable, energy-dense, solid fuel.

The major chemical fractions of lignocellulosic biomass are lignin, cellulose, hemicellulose, aqueous extractives, and ash (Goering

and Van Soest, 1970). Monomeric sugars (mainly glucose and fructose) along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides are the main components of aqueous solubles in biomass (Minowa et al., 1998). Hemicellulose is a heteropolymer, composed of sugar monomers, including xylose, mannose, glucose, and galactose with  $\beta$ -(1–4) glucosidic bonds. The ratios of these monomers in hemicellulose vary dramatically within a given feedstock, but their cumulative content is almost identical in most types of wood (Garrote et al., 1999). Cellulose, a polysaccharide of glucose with  $\beta$ -(1–4) glucosidic bonds, is the most abundant chemical component of biomass (Cuiping et al., 2004). Lignin is a high molecular weight cross-linked polymer of phenyl propane derivatives (Peterson et al., 2008). Every biomass has these chemical components, however, their contents vary in each feedstock (Cuiping et al., 2004).

Hydrothermal carbonization (HTC) also known as wet torrefaction, is a prominent pretreatment process for biomass enhancement (Acharjee et al., 2011; Funke and Ziegler, 2010; Kobayashi et al., 2009; Yan et al., 2009). In HTC, biomass is treated with hot compressed water, resulting in three products: gases, aqueous products,

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and a solid product sometimes known as hydrochar, and referred to here as HTC biochar. Typical reaction temperatures are in the range of 200–275 °C, and pressures are maintained above the saturation pressure to ensure the liquid state of water. In this temperature range, the ionic constant of subcritical water increases nearly two orders of magnitude and liquid water behaves as a non-polar solvent (Bandura and Lvov, 2006). The gaseous products from HTC represent about 10% of the original biomass, depending on the temperature, consisting mainly of CO<sub>2</sub>, while the aqueous soluble compounds are primarily sugars, acetic acid, and other organic acids (Hoekman et al., 2011). The solid product contains about 41–90% of the mass and 80–95% of the calorific value of the original feedstock (Garrote et al., 1999; Yan et al., 2010). HTC biochar is friable and more hydrophobic than the original biomass (Acharjee et al., 2011; Libra et al., 2011).

Aqueous extractives are readily extracted in hot compressed water. Hemicellulose, a non-crystalline polymer with a lack of repeating  $\beta$ -(1–4)-glycosidic bonds, has little resistance to hydrolysis or hydrothermal extraction in hot compressed water (Bobleter, 1994; Peterson et al., 2008). Mok and Antal (1992) found that an average of 90% of the hemicellulose degrades into monomeric sugars at 34.5 MPa and 200–230 °C (Mok and Antal, 1992). It is reported that the activation energy of hemicellulose degradation is 82–156 kJ/mol for various biomass materials in the temperature range of 145–190 °C assuming a first order reaction (Garrote et al., 1999; Grénman et al., 2011; Mittal et al., 2009).

Unlike hemicellulose, cellulose has repeating  $\beta$ -(1–4)-glycosidic bonds between glucose, which allows strong intra- and inter-molecular hydrogen bonds to form, making cellulose crystalline, resistant to swelling in water, and resistant to attack by enzymes (Peterson et al., 2008). However, subcritical water at elevated temperatures (>230 °C) can disrupt the hydrogen bonds and crystalline structure, and thus hydrolyze the  $\beta$ -(1–4)-glycosidic bonds to form glucose monomers (Funke and Ziegler, 2010). The  $\beta$ -(1–4)-glycosidic bonds of both hemicellulose and cellulose can be broken using acidic liquid media at elevated temperatures (Lynam et al., 2011). Bobleter, (1994), showed first order reaction kinetics for cotton cellulose degradation with an activation energy of 129 kJ/mol in the temperature range of 215–274 °C (Bobleter, 1994). However, Peterson et al., (2008), plotted data from several literature sources using first order Arrhenius kinetics and found the activation energy of cellulose to be 215 kJ/mol in a temperature range of 210–370 °C (Peterson et al., 2008).

Lignin, with phenylpropane derivatives such as *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, is a cross linked polymer which is stable in hot compressed water at temperatures below 260 °C (Zhang et al., 2008).

Owing to the molecular structure of lignocellulosic biomass, the complex reaction scheme in HTC could involve many different reactions. The main objective of the HTC is to economically convert raw biomass into a feedstock with improved physical and chemical properties for combustion and gasification. Hence, the solid char product after HTC is of the most interest. The kinetics of carbonization during HTC determine the required residence time and reactor volume, and are therefore of great importance for further process design and economic evaluation. The objective of this work is determination of the mass loss kinetics of HTC of wood by experiments in a specially-designed two-chamber reactor.

## 2. Methods

### 2.1. Biomass

Loblolly pine (*Pinus taeda* L.) (Alabama, USA) was used in all experiments reported here. A fiber analysis was measured according the Van Soest method (Goering and Van Soest, 1970). On a dry

mass basis, the biomass consists of 11.9% hemicellulose, 54.0% cellulose, 25.0% lignin, 8.7% water-extractives and 0.4% ash (Reza, 2011). Pine samples were milled to a particle size range of 0.5 ± 0.2 mm, and dried at 105 °C for 24 h prior to the experiment.

### 2.2. Hydrothermal carbonization

HTC experiments are typically done in heavy steel reactors to hold the high pressure with long heating times (Funke and Ziegler, 2010; Yan et al., 2009). As the reactor is heated, it is likely that HTC reactions are initiated well before the desired reaction temperatures are reached. This makes the precise study of mass-loss kinetics difficult. To overcome this difficulty, a specially-designed two-chamber reactor was built, which allows very rapid heating of the biomass reactant during HTC.

#### 2.2.1. Reactor set-up

Fig. 1a shows a schematic diagram of the reactor system, including a two-chamber reactor, a radiant heater, a temperature indicator, and a PID temperature controller. Two similar double-chamber reactors were designed and built for this kinetic study; they are referenced as reactor A and reactor B. The bottom chamber (volume: 20 mL for reactor A and 200 mL for reactor B) and the top chamber (volume: 10 mL for reactor A and 20 mL for reactor B) were connected with Swagelok ball valves (Sunnyvale, CA), which can handle high temperatures (up to 454 °C) and high pressures (up to 6.9 MPa). A ceramic radiant heater of 600 W (Omega Engineering, Stamford, CT) was used to heat the bottom chamber of the reactor, where the HTC reaction actually occurs. Two thermocouples (inside and outside the bottom chamber) were used, while only outside temperature was controlled by the controller. Since there was a constant temperature difference (typically 90 °C) between the chamber-wall temperature and the chamber-inner temperature, the controller set point input was set at 90 °C higher than the desired HTC temperature. A water cooling coil was placed on the top chamber to keep the biomass sample cool while heating the bottom chamber. While the valve is closed, the two chambers are thermally separated. For safety reasons, a pressure relieve valve was installed in the two-chamber reactor.

#### 2.2.2. Experimental procedure

The procedure for HTC using the two chamber reactor is shown in Fig. 1b–d. For reactor A, 15 mL of de-ionized water was loaded into the bottom chamber (30 mL was used for reactor B), and the ball valve was closed to almost 90%. A biomass sample (0.2 g for reactor A and 1 g for reactor B) was wrapped into a close-ended cylindrical-shaped capsule (20 mm height and 10 mm diameter). Stainless steel screen (320 mesh), was used for making the sample holder. The biomass capsule was placed into the top chamber and the reactor was closed. After entering the bottom chamber, the sample holder allowed the liquid to rapidly wet the solid, and prevented the biomass from escaping. Nitrogen was charged for 2 min into the closed reactor at a rate of 80 mL (STP)/min, and then the pressure was released for 10–15 s. This process was repeated for five times to remove oxygen from the reactor. The ball valve was then fully closed.

The bottom chamber's external wall was heated to 115 °C above the reaction temperature, while the upper chamber was maintained at room temperature by cooling water. Once the wall temperature reached the desired value, the ball valve was fully opened, letting the capsule fall from the upper to the bottom chamber, which was then closed within 3–5 s. The rapid pressure drop experienced in the lower chamber, caused by opening the valve to the upper chamber, resulted in cooling by adiabatic expansion. This caused the water temperature to drop about 25 °C. Therefore, the water in the bottom chamber reached the desired

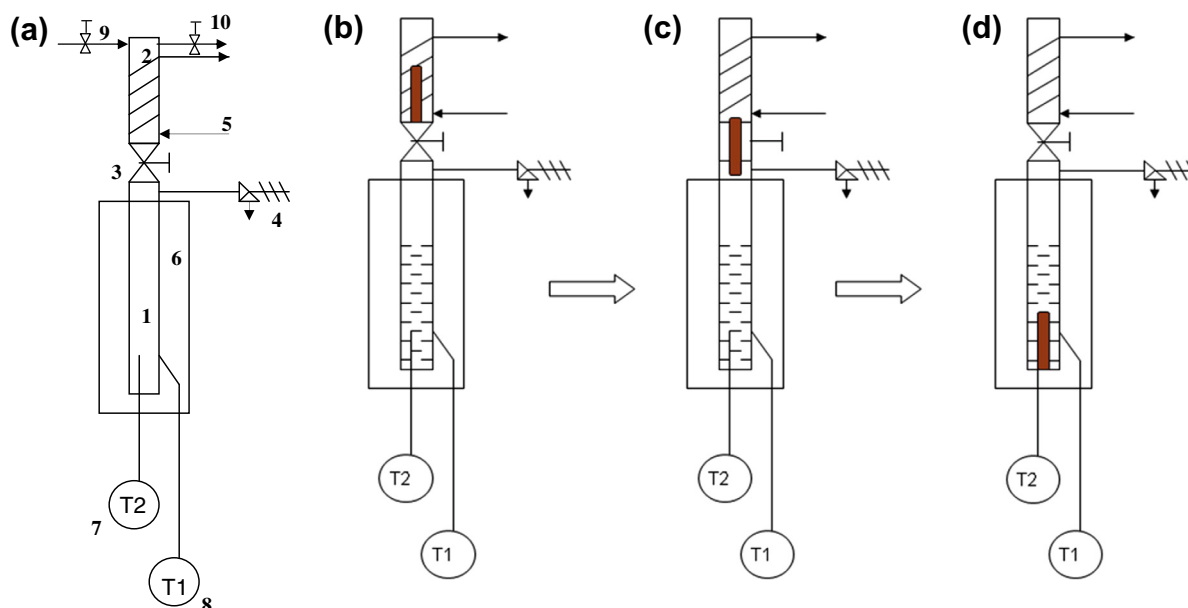


**Fig. 1.** Schematic of the two-chamber reactor system, and method for placing biomass in hot compressed water for rapid sample heating. (a) The components: (1) bottom chamber where reaction is performed; (2) top chamber where reactant is held while bottom chamber heats; (3) ball valve; (4) pressure relief valve; (5) water-cooling coil; (6) radiant heater; (7) temperature indicator; (8) PID temperature controller; (9) N<sub>2</sub> in; (10) N<sub>2</sub> out. (b) Water is heated in lower chamber while sample stays cool in top chamber, (c) open the ball valve allowing sample to drop into the bottom chamber, (d) sample is drops into the hot water and the ball valve is closed.

reaction temperature. Hydrothermal carbonization started as soon as the biomass contacted the hot water. After the desired HTC time (e.g., 15, 30, 45 s, 1–5 min), the reactor was quickly removed from the radiant heater and immersed into an ice-water bath to quench the reaction. Internal reactor temperature drops below 180 °C within about 10 s, after which it is assumed that all reactions have stopped. Once the reactor reached room temperature after 2–5 min, the biomass capsule was taken out of the bottom chamber, and washed with 50 mL of water to remove the aqueous chemicals. The wet pretreated biomass was dried at 105 °C for 24 h before further analysis. All experiments were performed at least three times; data reported are averages.

### 2.3. Energy content

The higher heating values (HHV) for the untreated biomass and the biochar products were measured in a Parr 1241 adiabatic oxygen bomb calorimeter (Moline, IL) fitted with continuous temperature recording. All samples (0.2 g each) were dried at 105 °C for 24 h prior to analysis, HHV results are reported on a dry, ash free basis.

### 2.4. Ash measurement

ASTM D 1102 method was followed for ash determination of HTC biochar. A dry sample of 0.5–2.0 g was heated in the muffle furnace at 575 °C for 24 h. Each experiment was done three times for better precision.

## 3. Results and discussion

### 3.1. Hydrothermal carbonization of loblolly pine

Hydrothermal carbonization of loblolly pine was performed in hot compressed water at temperatures of 200, 230, and 260 °C in reactor A. The experimental data were collected at eleven intervals: 15, 30, 45 s, 1–5, 10, 20, and 30 min. The experimental results

of hydrothermal carbonization of loblolly pine are summarized in Table 1 and shown in Fig. 2. The mass yield, energy densification ratio, and energy yield are defined as below.

$$\text{Mass yield} = \frac{\text{Mass of dried pretreated biochar}}{\text{Mass of dried raw biomass}} \times 100\% \quad (1)$$

$$\text{Energy densification ratio} = \frac{\text{HHV of dried pretreated biochar}}{\text{HHV of dried raw biomass}} \quad (2)$$

$$\text{Energy yield} = \text{Mass yield} \times \text{Energy densification ratio} \quad (3)$$

After the first minute, the mass yields drop to 81%, 66%, and 56% at 200, 230, and 260 °C, respectively. With increased reaction times, mass yield changes less dramatically with the increasing reaction temperature. At 5 min, the mass yields reach 64%, 58% and 54% at 200, 230 and 260 °C, respectively. (Yan et al., 2009) reported mass yields of 88.7%, 70.6% and 57% for 5 min HTC reactions at identical temperatures, also using loblolly pine as biomass (Yan et al., 2009). A likely explanation for the lower mass yields reported here might be the dilution of aqueous extractives present in the solids. In this study, the water/biomass ratio, as well as solid biochar treatment after the HTC, were different from the approach used earlier by Yan et al., (2009). Subcritical water degrades aqueous extractives and decomposes hemicellulose into its monomers below 200 °C, and thus produces a sugar solution (Antal et al., 1990; Hoekman et al., 2011; Keiluweit et al., 2010). Sugars or furfural derivatives can be adsorbed on the solid biochar, thus contributing to the recovered mass (Keiluweit et al., 2010). At higher temperatures the sugars may be further degraded resulting in less deposition. The similar mass yield at 260 °C, compared to the other reaction temperatures, might be evidence of sugar degradation.

Mass yield is nearly constant at higher temperatures after a short period of time. For example, HTC 260 mass yield was 56% after the first minute and it decreased further only to 54% for reaction times longer than 1 min. This could indicate completion of the solid-phase HTC reactions. Cellulose in hydrothermal media has

**Table 1**Hydrothermal carbonization of loblolly pine. The higher heating value (HHV) of raw loblolly pine is 19.22 MJ kg<sup>-1</sup>.

| Temperature (°C) | Time (s) | Mass yield (%) | HHV (MJ kg <sup>-1</sup> ) | Energy densification ratio | Energy yield (%) |
|------------------|----------|----------------|----------------------------|----------------------------|------------------|
| 200              | 15       | 90.13 ± 1.8    | 19.5 ± 0.3                 | 1.01                       | 91.2             |
|                  | 30       | 85.02 ± 1.7    | 19.5 ± 0.7                 | 1.02                       | 86.4             |
|                  | 45       | 82.45 ± 1.7    | 19.7 ± 0.6                 | 1.03                       | 84.6             |
|                  | 60       | 81.44 ± 2.2    | 19.9 ± 1.4                 | 1.03                       | 84.3             |
|                  | 120      | 76.80 ± 2.1    | 20.4 ± 1.4                 | 1.06                       | 81.6             |
|                  | 180      | 74.45 ± 1.8    | 20.9 ± 0.2                 | 1.09                       | 81.0             |
|                  | 240      | 69.59 ± 0.9    | 21.6 ± 0.6                 | 1.13                       | 78.3             |
|                  | 300      | 63.88 ± 0.1    | 21.9 ± 0.9                 | 1.14                       | 72.8             |
| 230              | 15       | 85.47 ± 2.2    | 19.8 ± 0.1                 | 1.03                       | 87.9             |
|                  | 30       | 76.50 ± 0.9    | 20.5 ± 0.2                 | 1.07                       | 81.5             |
|                  | 45       | 70.19 ± 0.8    | 21.1 ± 0.2                 | 1.10                       | 76.9             |
|                  | 60       | 66.48 ± 0.9    | 22.0 ± 0.5                 | 1.14                       | 76.0             |
|                  | 120      | 63.65 ± 0.5    | 22.7 ± 0.2                 | 1.18                       | 75.3             |
|                  | 180      | 62.70 ± 1.5    | 23.2 ± 0.4                 | 1.21                       | 75.6             |
|                  | 240      | 59.51 ± 1.0    | 23.4 ± 0.8                 | 1.22                       | 72.4             |
|                  | 300      | 58.04 ± 1.1    | 23.4 ± 0.8                 | 1.22                       | 70.8             |
| 260              | 15       | 85.83 ± 1.9    | 21.2 ± 0.9                 | 1.10                       | 94.5             |
|                  | 30       | 73.79 ± 0.9    | 22.0 ± 0.2                 | 1.14                       | 84.3             |
|                  | 45       | 63.69 ± 1.1    | 24.0 ± 1.0                 | 1.25                       | 79.5             |
|                  | 60       | 55.90 ± 1.4    | 26.0 ± 1.4                 | 1.35                       | 74.4             |
|                  | 120      | 54.94 ± 4.2    | 26.4 ± 1.2                 | 1.37                       | 76.8             |
|                  | 180      | 54.70 ± 4.9    | 26.5 ± 1.1                 | 1.38                       | 76.3             |
|                  | 240      | 54.60 ± 3.4    | 26.6 ± 0.4                 | 1.38                       | 75.6             |
|                  | 300      | 54.30 ± 4.5    | 26.2 ± 1.8                 | 1.36                       | 74.3             |

been reported to produce 50–60% biochar in the temperature range of 200–275 °C (Funke and Ziegler, 2010; Keiluweit et al., 2010).

For HTC 200 and 230, the mass yield decreased with increasing reaction time to approach a single point (54%) (Fig. 2a). Lynam et al. (2011) reported the pH effect on HTC reaction (Lynam et al., 2011). With the introduction of an acidic environment, it is possible to degrade cellulose at temperatures lower than 230 °C. As the degradation of hemicellulose proceeds, aqueous extractives produce organic acids, which could contribute to degradation of cellulose at temperatures as low as 200 °C. This could explain having the same mass yield for a longer period of time regardless the HTC temperature.

Energy value for the HTC biochar produced at different temperatures and different times are shown in Fig. 2b and Table 1. Energy value follows an inverse trend as the mass yield. At 200 °C, the HHV of pretreated biomass increases slowly and linearly with increasing reaction time. At 230 and 260 °C, there is significant energy densification occurring during the first and second minutes of hydrothermal carbonization. The HHV is similar for all HTC 260 biochars at and after 1 min. HTC 230 and 200 have a higher HHV than that reported by Yan et al., (2009). As discussed earlier this may be explained by the reduced content of soluble compounds deposited in the solid, due to increased dilution, and due to sample washing. Some extractives have lower HHV than the biochar, and extractive concentrations are lower in this study than in the literature (Reza et al., 2012; Yan et al., 2010). After 5 min of hydrothermal carbonization, the energy densification ratios are 1.14, 1.22 and 1.36 at temperatures of 200, 230 and 260 °C, respectively.

### 3.2. Kinetic model for hydrothermal carbonization

Each of the four major biomass fractions (lignin, cellulose, hemicellulose, and aqueous extractives) of a lignocellulosic biomass will react distinctly in the presence of a specific hydrothermal condition (Peterson et al., 2008). All the activation energies discussed previously in the literature were reported for the pure components, but lignocellulosic biomass consisting of all compounds together, may experience different activation energies. One reaction can affect the other, resulting in a change of

activation energy for the individual components. A simple kinetic model, consisting of two parallel first-order reactions is proposed here for hydrothermal carbonization of lignocellulosic biomass.

Because aqueous extractives (including starch, simple sugars, protein) are very reactive in hydrothermal media, an instantaneous reaction is assumed for them, with the products consisting of aqueous chemicals and gases in this simple kinetic model (Peterson et al., 2008). In the proposed kinetic model, hemicellulose is said to decompose in a first-order reaction, which results in two types of products: aqueous chemicals and gases. Cellulose is also said to decompose by a first-order reaction, which produces a solid product, aqueous chemicals, and gases. The solid product here is referred to as B<sub>c</sub>, and has characteristics similar to lignin and can entrap the extractives inside it (Funke and Ziegler, 2010; Peterson et al., 2008). It could be part of the high crystallinity cellulose remaining at the temperatures investigated herein, or may consist of cross-linked polymers with entrapped extractives (Antal et al., 1990; Jacobsen and Wyman, 2000). In this simplified kinetic model, lignin is assumed to be inert at the temperatures investigated. Any extractives entrapped in the biochar will be included as a part of B<sub>c</sub>. The reactions can be written as the following:



where AE, S, G, H, C, and B<sub>c</sub>, represent aqueous extractives, aqueous chemicals, gases, hemicelluloses, cellulose, and solid products from cellulose decomposition, respectively. If hemicellulose (12% in raw loblolly pine) and aqueous extractives (9%) react completely to liquid or gas phase products, while cellulose (54%) reacts to make 50% biochar, and lignin is inert, then theoretically the mass yield would be 52.5%. Ash in unpretreated loblolly pine and HTC biochar was very similar and small (0.5%) and it was constant throughout the study (Yan et al., 2010). The mass yield of solid products from cellulose is denoted by the parameter  $\beta$  in the third reaction. The rates of decomposition of both hemicellulose (H(t)) and cellulose

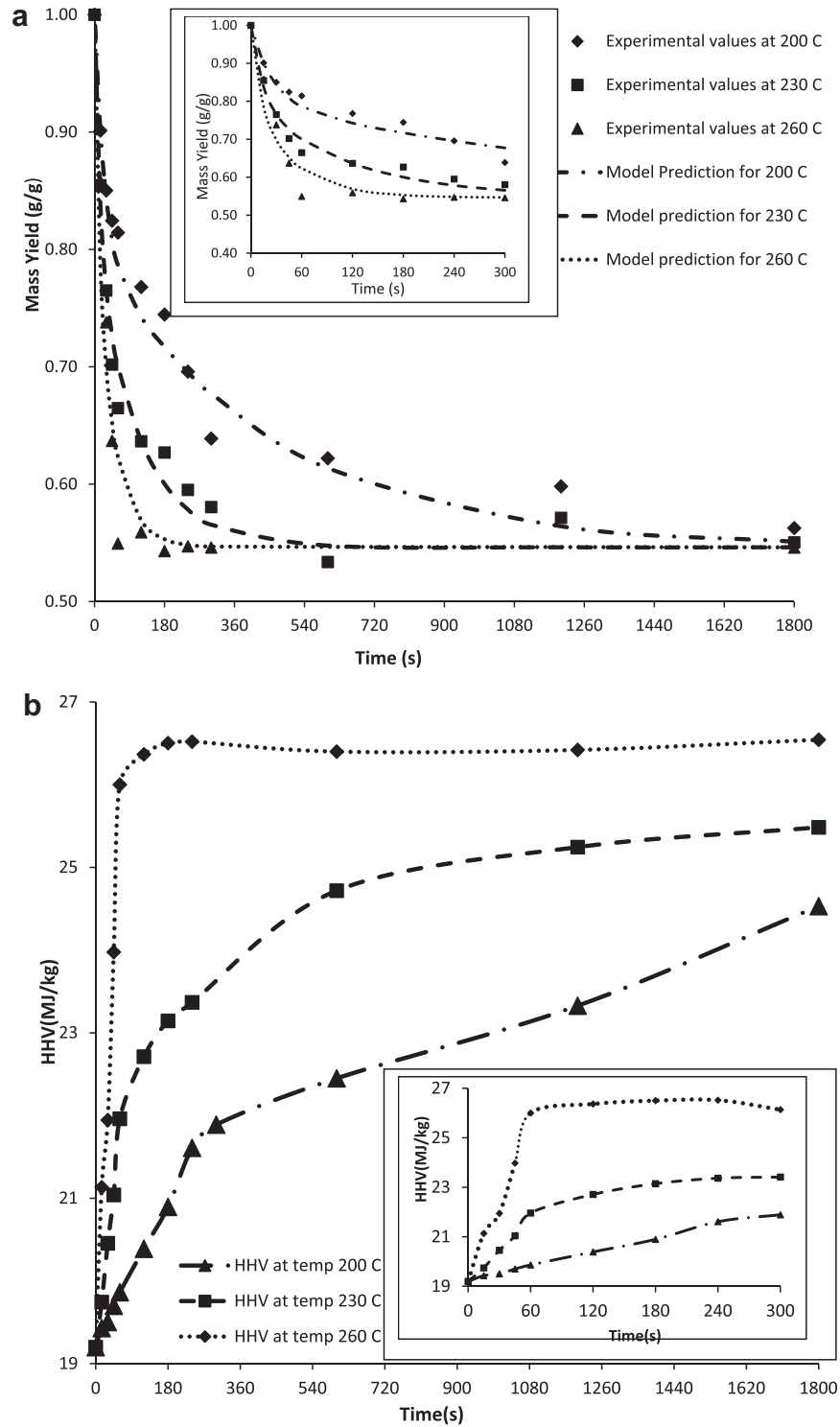


**Fig. 2.** (a) Mass yield as a function of time at three reaction temperatures. Inset is the mass yield from initial to 5 min where the rapid degradation occurs. Curves shown are the kinetic model with parameters fitted. (b) Energy content of HTC loblolly pine as a function of time at three reaction temperatures. The higher heating value (HHV) of raw loblolly pine is  $19.22 \text{ MJ kg}^{-1}$ . Curves indicate trends in measured data. Inset is the HHV from initial to 5 min where the rapid degradation occurs.

( $C(t)$ ) are both described by the first order reaction kinetics, where  $k_1$  and  $k_2$  are the rate constants for the two reactions.

$$\frac{dH(t)}{dt} = -k_1 H(t) \quad (7)$$

$$\frac{dC(t)}{dt} = -k_2 C(t) \quad (8)$$

The system of equations can be solved analytically. Integration of the differential equations, with the initial mass at time zero, gives the expression for the functions of  $H(t)$ ,  $C(t)$ , and  $B_c(t)$ , which are shown by Eqs. (9)–(11). Since lignin is considered to be an inert component, the function of  $L(t)$  is expressed as a constant Eq. (12).

$$H(t) = H_0 e^{-k_1 t} \quad (9)$$

$$C(t) = C_0 e^{-k_2 t} \quad (10)$$

$$B_c(t) = \beta C_0 (1 - e^{-k_2 t}) \quad (11)$$

$$L(t) = L_0. \quad (12)$$

where  $H_0$ ,  $C_0$ , and  $L_0$  represent the initial mass of hemicellulose, cellulose, and lignin, respectively. If  $M(t)$  represents the mass of unreacted biomass plus solid-phase reaction products at time  $t$ ,  $M(t)$  can be written by Eq. (13).

$$M(t) = H(t) + C(t) + B_c(t) + L(t) \quad (13)$$

To express the mass yield of biochar  $Y(t)$ , Eq. (13) can be rewritten as Eq. (14).

$$Y(t) = \frac{M(t)}{M_0} = Y_{H0} e^{-k_1 t} + Y_{C0} e^{-k_2 t} + \beta Y_{C0} (1 - e^{-k_2 t}) + Y_{L0} \quad (14)$$

where  $Y_{H0}$ ,  $Y_{C0}$ , and  $Y_{L0}$  represents initial mass fraction of hemicellulose, cellulose, and lignin in dry lignocellulosic biomass feedstock, respectively.

### 3.3. Kinetic model evaluation for hydrothermal carbonization

For loblolly pine, the initial mass content of hemicellulose, aqueous extractives, cellulose, and lignin are discussed in Section 2.1. To determine the mass yield of biomass by Eq. (14), the value of  $\beta$  is needed at any time  $t$ . If  $t$  tends to infinity then Eq. (14) will be written as Eq. (12), without considering aqueous extractives:

$$\lim_{t \rightarrow \infty} Y(t) = \beta Y_{C0} + Y_{L0} \quad (15)$$

Eq. (15) is independent of HTC temperature if  $\beta$  is a temperature-independent parameter. To evaluate  $\beta$  and determine its dependency on HTC temperature, HTC reactions for extended periods (10, 15, and 30 min) were performed at all three temperatures and are shown in Fig. 2a. The results show that the mass yields of pretreated biomass at the three temperatures used approach the same value of 54% after 30 min of HTC. Substituting the known values gives a single value for  $\beta$ , equal to 0.54, independent of temperature in the range of 200–260 °C. This indicates that, as cellulose degrades, 54% of its mass is a solid-phase product.

The preceding analysis leaves  $k_1$  and  $k_2$  as the only unknown parameters in Eq. (14). The best fit for rate constants can be obtained by minimizing the objective function  $F(k_1, k_2)$ .

$$F(k_1, k_2) = \sum_{i=1}^{11} (Y_i^{\text{experimental}} - Y_i^{\text{model}}(k_1, k_2))^2 \quad (16)$$

where  $Y_i^{\text{experimental}}$  represents the experimental mass yield,  $Y_i^{\text{model}}$  represents the mass yield as calculated in Eq. (14), and  $i$  represents each of 11 reaction times. The function  $F$  was minimized with respect to  $k_1$  and  $k_2$  at each of the three reaction temperatures, with values of both rate constants reported in Table 2. The objective function was minimized using the conjugate gradient method in Microsoft Excel solver. Fig. 2a shows the model prediction with the experimental values. The two parallel first order reactions for

**Table 2**  
First-order rate constants found by minimizing the objective function shown in Eq. (16). These values were used in Eq. (14) to plot the smooth curves for mass yield shown in Fig. 2a.

| Temperature (°C) | $k_1$ (s <sup>-1</sup> ) | $k_2$ (s <sup>-1</sup> ) |
|------------------|--------------------------|--------------------------|
| 200              | 0.04                     | 0.0022                   |
| 230              | 0.07                     | 0.0085                   |
| 260              | 0.09                     | 0.0200                   |

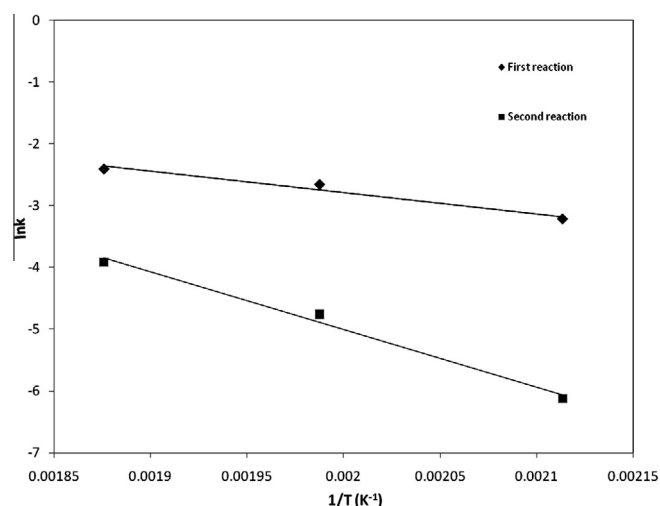


**Fig. 3.** Arrhenius plot for  $k_1$  and  $k_2$ , first-order rate constants for degradation of hemicellulose and cellulose, respectively. Activation energies are 29 and 77 kJ/mol, respectively. Pre-exponential factors are 58.6 and  $8.24 \times 10^5$  s<sup>-1</sup>.

**Table 3**

Activation energy for decomposition of hemicellulose ( $E_1$ ) and for decomposition of cellulose ( $E_2$ ), calculated by using only mean values given in Table 2 (deterministic), and calculated from the Monte Carlo analysis (statistical).

|               | $E_1$ (kJ/mol) | $E_2$ (kJ/mol) |
|---------------|----------------|----------------|
| Deterministic | 29             | 77             |
| Statistical   | 30             | 73             |

hemicellulose and cellulose seems to predict with reasonable accuracy the mass yield of HTC in the temperature range of 200–260 °C.

### 3.4. Kinetic parameters estimation for hydrothermal carbonization

An Arrhenius plot for both  $k_1$  and  $k_2$  is shown in Fig. 3. Activation energies and pre-exponential factors are obtained from the slopes of Fig. 3; the activation energies ( $E_1$  and  $E_2$  in Table 3) are 29 kJ mol<sup>-1</sup> for hemicellulose ( $k_1$ ), and 77 kJ mol<sup>-1</sup> for cellulose ( $k_2$ ). The higher activation energy for cellulose compared to that of hemicellulose is consistent with data reported elsewhere (Garrote et al., 1999; Peterson et al., 2008), indicating the greater recalcitrance of cellulose. The numerical values for activation energies are smaller than those of the pure hemicellulose and cellulose (129–215 kJ/mol) in this temperature range (Grénman et al., 2011; Peterson et al., 2008). Instantaneous degradation of aqueous extractives likely reduces the pH of the solution and thus enhances degradation of hemicelluloses and cellulose (Lynam et al., 2011), while hemicellulose degradation results in even greater acid production, further catalyzing cellulose reactions. As a result, the individual activation energies for both hemicellulose and cellulose are lower than those for the pure forms not encased in a lignocellulosic biomass package. Lignin, in this simple kinetic model, is assumed inert but as it is observed that the activation energies of hemicellulose and cellulose are lower in lignocellulosic biomass than their pure form, so lignin activation energy might also be reduced, and thus it is possible that a part of lignin is degraded at higher temperatures. So, a further kinetic study including lignin degradation might predict the degradation model better than this study.

Torrefaction is another practice for thermally carbonizing lignocellulosic biomass. Prins et al. (2006) reported a kinetic study of torrefaction of lignocellulosic biomass assuming similar first-order reactions for hemicelluloses and cellulose, and reported activation energies of 76 and 152 kJ mol<sup>-1</sup>, respectively (Prins et al., 2006).

Compared to the (dry) torrefaction results (Yan et al., 2012), HTC kinetics in this study are very fast, likely due to the reactivity of high-temperature water.

### 3.5. Error analysis of kinetics parameters

The activation energy calculation involves several steps that include use of measured and calculated variables containing various experimental errors and uncertainties. A simple Monte Carlo simulation method is applied here to understand how each calculation step could influence the overall results and allows us to quantify the error in calculated activation energies reported above. The Monte Carlo method is a stochastic method for analyzing uncertainty propagation, where the goal is to determine how random variation, lack of knowledge, or error affects the sensitivity, performance, or reliability of the system that is being modeled (Metropolis and Ulam, 1949). Three direct measurements of weight were used to calculate each value of mass yields reported in Table 1, each with an associated experimental uncertainty. For this error analysis, 100 random uniform numbers were generated for each measured value, centered around the recorded value; this means that the mass yield could be calculated 100 times. Each mass yield reported in Table 1 was measured three times; thus for each condition of time and temperature, the mass yield was calculated 300 times for this error analysis, each an equally likely value of the true mass yield. A new normal population distribution was obtained

from the stochastically data. Using the Nonlinear Quasi-Newton solution method in Mathcad 15, the best fit values for rate constants were determined for each set of data at a single temperature. Greater detail of the error analysis method is provided in the Supplemental materials.

The final result of this exercise was a distribution of values for activation energies for both  $k_1$  and  $k_2$ , shown in Fig. 4. Mean values and standard deviations for both reaction constants were calculated from those distributions. The mean activation energy for hemicellulose degradation ( $k_1$ ) was 30 kJ/mol with a standard deviation of 12 kJ/mol, and for cellulose was 73 kJ/mol with a standard deviation of 6 kJ/mol. The variance for the activation energy for  $k_1$  (hemicellulose) was relatively high (40%), while that for  $k_2$  was about 8%. As discussed earlier, hemicellulose degradation is very rapid and the effect can be observed only during the first 1–2 min at lower temperatures. It is possible that the experiments done in such short times involved more errors than those done in longer time periods. Thus, numerical evaluation of the first-order rate constant of hemicellulose degradation is subject to a high degree of uncertainty. The mean values found from this Monte Carlo simulation were similar to those found by deterministic calculations, as shown in Fig. 3, and are compared in Table 3. In both cases, the mean values found from deterministic calculations (using only mean mass yields) are within a single standard deviation of the mean found from the Monte Carlo simulation.

### 3.6. Particle size effect on hydrothermal carbonization

Both mass transfer and intrinsic reaction kinetics may play a role in determining the overall rate of the mass degradation reactions of lignocellulosic biomass in hydrothermal media. The HTC reactions occur within the pores of the biomass and thus, hot water must enter the pores, while at the same time, the aqueous products must leave the pores. Mass transfer of reaction products from the pores could be a rate limiting step, since the reaction kinetics seems to be fast, as discussed above. Below, the effects of mass transfer are evaluated by measuring reaction rates with different particle size for short contact times.

For this study, reactor B was used to perform HTC at 230 °C and 1 min of reaction time with three particle sizes. Table 4 shows the experimental conditions, and a summary of the relevant results. For an identical time, temperature, and biomass, the mass yield is increasing with increasing particle size, which implies that mass transfer effects may be rate limiting. A simple model has been developed to account for simultaneous effects of mass transfer and reaction kinetics for HTC reactions. In this model, cellulose degradation was assumed to represent all HTC reactions, since hemicellulose can be assumed to be essentially degraded after 1 min at 230 °C, while lignin is relatively inert. Other key assumptions for the mass transfer analysis are the following:

- Reaction is said to occur on the surface of a cylindrical pore extending through the particle to the particle surface, with length equal to the particle diameter.
- Mass diffusion and reaction occur on the pore surface and there is no radial mass transfer; mass transport is modeled to occur only in the axial direction of the pore. The rate is independent of pore diameter.
- Glucose is the only fluid product of cellulose degradation, and glucose alone is transported out of the pore during reaction.
- The system is modeled as steady state. Strictly speaking, this is incorrect, since the solid reactant is being continuously consumed, and the rate of reaction decreases continuously. However, this is a pseudo-steady state assumption, in which

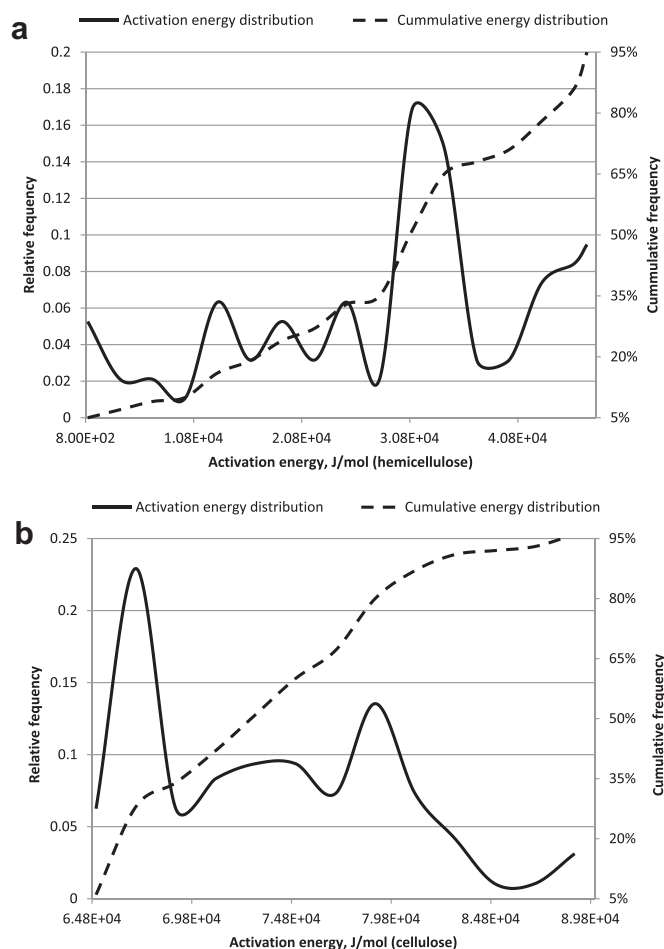


**Fig. 4.** (a) Distribution of values for activation energy of hemicellulose degradation, ( $E_1$ ). The mean value is 30 kJ/mol. Shown is the 90% confidence interval. (b) Distribution of values for activation energy of cellulose degradation, ( $E_2$ ). The mean value is 73 kJ/mol. Shown is the 90% confidence interval.

**Table 4**

Effect of particle size on hydrothermal carbonization at 230 °C and 1 min reaction time.

| Tyler mesh | Average particle diameter (mm) | Average particle length (mm) | Mass yield (%) | Thiele modulus |
|------------|--------------------------------|------------------------------|----------------|----------------|
| 14–28      | 0.88                           | 3.5                          | 68.6           | 1.7            |
| 10–14      | 1.4                            | 4.2                          | 69.9           | 2.0            |
| 8–10       | 2.1                            | 5.1                          | 71.4           | 2.4            |

**Table 5**

Physical properties used for calculation of Thiele modulus.

| Variable              | Description                                                        | Value                       | Refs.                       |
|-----------------------|--------------------------------------------------------------------|-----------------------------|-----------------------------|
| $T_0$                 | Reference temperature                                              | 25 °C                       | –                           |
| $\mu(T_0)$            | Viscosity of water at reference temperature                        | 8.89 E–4 Pa s               | Levenspiel, (1999)          |
| $D_{\text{eff}}(T_0)$ | Effective diffusivity of glucose at reference temperature          | 6.735E–10 m <sup>2</sup> /s | Goldberg and Tewari, (1988) |
| $\alpha$              | Stoichiometric production of glucose from degradation of cellulose | 0.4                         | This work                   |
| $t$                   | Time                                                               | 60 s                        | –                           |
| $T$                   | Reaction temperature                                               | 230 °C                      | –                           |

it is assumed that the pore geometry and rate of reaction change only slowly relative to the time required for diffusion through a pore.

A steady-state material balance on glucose in a differential volume in a single cylindrical pore gives:

$$\text{Rate of mass in} - \text{Rate of mass out} + \text{Rate of production} = 0 \quad (17)$$

which can be written in the following dimensionless form, assuming constant diffusivity and dilute concentration.

$$\frac{d^2\psi}{d\lambda^2} + \phi^2 = 0 \quad (18)$$

$$\phi^2 = \frac{L^2 \alpha k_2 e^{-k_2 t}}{D_{\text{eff}}}$$

$\Psi$  is dimensionless concentration, and  $\lambda$  is the dimensionless axial position.  $D_{\text{eff}}$  is the effective diffusivity,  $L$  is the pore length (particle diameter) reported in Table 4,  $k_2$  the rate of cellulose degradation, and  $\alpha$  the stoichiometric production of glucose from cellulose. Note that the glucose is a product of reaction, not a reactant, and its rate of production is first order in cellulose; that is, the rate is independent of glucose concentration. This is mathematically similar to a zero order reaction, from the perspective of glucose. Next, the dimensionless Thiele modulus  $\Phi$  is evaluated to identify the rate limiting step (Minowa et al., 1998).

The temperature effect on diffusivity ( $D_{\text{eff}}$ ) is taken into account by applying the Stokes–Einstein equation for liquid diffusion, as follows:

$$D_{\text{eff}}(T) = D_{\text{eff}}(T_0) \left( \frac{T}{T_0} \frac{\mu(T_0)}{\mu(T)} \right) \quad (19)$$

here  $T$  and  $T_0$  represent the reaction temperature and a reference temperature at which the viscosity  $\mu(T_0)$  and diffusivity  $D_{\text{eff}}(T_0)$  are known. Numerical values needed to evaluate  $D_{\text{eff}}$  and  $\Phi$  are provided in Table 5, and the computed values of  $\Phi$  are given in Table 4.

This is similar to the Thiele modulus for a zero-order porous catalyst reactive system (Levenspiel, 1999). For  $\Phi < 0.4$ , the concentration of reactant does not drop appreciably within the pore;

thus pore diffusion offers negligible resistance. This means that a short pore, a slow reaction, or rapid diffusion exists, with all three factors tending to lower the resistance to diffusion. For  $\Phi > 4$ , the concentration of reactant drops rapidly to zero on moving into the pore; hence diffusion strongly influences the rate of reaction (Levenspiel, 1999). The effects of both reaction and diffusion are prominent in HTC, as they are in the range of 1.7–2.4. As temperature increases, both mass transfer and reaction increase; since the Thiele modulus is increasing with temperature, it is concluded that the overall reaction rate is more dominated by mass transfer considerations at higher temperatures. From the analogy of Thiele modulus it can be said that mass diffusion and cellulose reaction rate both play important roles in HTC reaction rate in the temperature range considered here.

## 4. Conclusions

The rate of mass loss of solid reactant in hydrothermal carbonization of woody biomass has been measured. Two parallel first-order reactions have been shown to describe accurately the mass yield for temperatures between 200 and 260 °C. Cellulose degradation ultimately yields 54% solid products at all temperatures. Cellulose degradation is described by a first order rate constant with activation energy 73 kJ/mol, and hemicellulose degradation has an activation energy of 30 kJ/mol. A careful analysis shows that both mass transfer and reaction kinetics consideration are important to predict the overall reaction rate.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2013.04.028>.

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